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Article

# Enhanced NH<sub>3</sub> Sensing Performance of Mo Cluster-MoS<sub>2</sub> Nanocomposite Thin Films via the Sulfurization of Mo<sub>6</sub> Cluster Iodides Precursor

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**Abstract:** The high-performance defect-rich MoS<sub>2</sub> dominated by sulfur vacancies as well as Mo-rich environments have been extensively studied in many fields, such as nitrogen reduction reactions, hydrogen evolution reactions, as well as sensing devices for NH<sub>3</sub>, which are attributed to the under-coordinated Mo atoms playing a significant role as catalytic sites in the defect area. In this study, the Mo cluster-MoS<sub>2</sub> composite was creatively synthesized through a one-step sulfurization process via H<sub>2</sub>/H<sub>2</sub>S gas flow. The Mo<sub>6</sub> cluster iodides (MIs) coated on the fluorine-doped tin oxide (FTO) glass substrate via the electrophoretic deposition method (i.e., MI@FTO) were used as a precursor to form a thin-film nanocomposite. Investigations into the structure, reaction mechanism, and NH<sub>3</sub> gas sensing performance were carried out in detail. The results indicated that during the gas flowing, the decomposed Mo<sub>6</sub> cluster iodides played the role of template and precursor, forming complicated Mo cluster compounds and eventually producing MoS<sub>2</sub>. These Mo cluster-MoS<sub>2</sub> thin-film nanocomposites were fabricated and applied as gas sensors for the first time. It turns out that after the sulfurization process, the response of MI@FTO for NH<sub>3</sub> gas increased three times while showing conversion from p-type to n-type semiconductor, which enhances their possibilities for future device applications.

**Keywords:** molybdenum octahedral cluster; molybdenum disulfide; sulfurization process; gas sensor

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## 1. Introduction

Graphene-like molybdenum disulfide (MoS<sub>2</sub>), with its well-known two-dimensional (2D) layered “sandwich” structure, has attracted significant attention over the years due to its unique electronic, optical, and chemical properties [1–4], which can be exploited in transistors [5,6], solar cells [7,8], catalysts [9–11], and sensors [12–14]. In this “sandwich” structure, one layer of molybdenum atoms is sandwiched between two layers of sulfur atoms. In the domain of catalysis, such MoS<sub>2</sub> three-layer structures have been widely investigated for their catalytic activity, which is strongly dependent on the edge sites [15].

To enhance the catalytic performance, researchers studied the synthesis of defect-rich MoS<sub>2</sub>, in which a sulfur vacancy that created the edge sites plays an important role [16–18]. Indeed, at the sulfur vacancy sites, the surrounding under-coordinated Mo atoms introduce gap states that facilitate N<sub>2</sub> absorption or hydrogen bonding, which improves the performance of the nitrogen reduction reaction (NRR) [19], hydrogen evolution reaction (HER) [20,21], as well as sensing [22–24].

With the development of defect engineering, researchers have devoted themselves to the synthesis of S vacancies defect-rich MoS<sub>2</sub> by using the hydrothermal route [25,26] and the chemical vapor deposition (CVD) method [27], which can control the sulfur-molybdenum ratio during the reaction to create defects. Alternatively, 2D-MoS<sub>2</sub> decorated with Mo clusters has started to attract some attention as a catalyst for the generation of acetylene via the CO hydrogenation reaction [28]. A higher electrocatalytic NRR activity has been theoretically proposed using Mo<sub>x</sub> clusters (x = 1–11) supported on MoS<sub>2</sub> [29]. Moreover, Jin et al. demonstrated the in situ fabrication of Mo<sub>6</sub>S<sub>6</sub>-nanowire-terminated edges in the monolayer MoS<sub>2</sub> [30] and developed a mass transport method for the formation of Mo chains induced by Mo clusters along the sulfur vacancy lines, aimed at tuning the defects and, thus, the materials' structure–property relationship in a well-controlled manner [31]. However, only a few studies have been conducted to generate MoS<sub>2</sub> by sulfurizing chalcogenide clusters, such as Mo<sub>6</sub>S<sub>2</sub>I<sub>8</sub>, as precursors [32,33].

In this study, we creatively pioneered the efficient synthesis route of Mo cluster-MoS<sub>2</sub> thin-film nanocomposites by a sulfurization process using Mo<sub>6</sub> cluster iodides as the precursors. Mo<sub>6</sub> cluster units are inorganic molecules containing six Mo atoms forming an octahedral skeleton that are connected by direct metal–metal bonds and are bonded with organic or inorganic ligands to stabilize the metal core. The interest in Mo<sub>6</sub> clusters-based compounds started with the discovery of the superconductivity in the Chevrel phases [34]. In recent decades, the optical properties and the chemical activity of Mo<sub>6</sub> clusters derived from their unique electronic structure [35–37] have been investigated and developed in many fields [38], such as luminescent [39–41], energy [42], and catalysis applications [43]. Among them, Nguyen et al. successfully developed a general process to coat metal-cluster-unit-based thin films, for example, Mo<sub>6</sub> cluster iodides (Cs<sub>2</sub>Mo<sub>6</sub>I<sub>14</sub>, CMI; more specifically, Cs<sup>+</sup><sub>2</sub>[{Mo<sub>6</sub>I<sub>8</sub>}I<sub>6</sub>]<sup>2-</sup>, where i and a represent the inner and apical iodide ligands, respectively, that surround the Mo<sub>6</sub> octahedra) on a fluorine-doped tin oxide (SnO<sub>2</sub>:F, FTO) glass substrate by the electrophoretic deposition (EPD) method [44]. This EPD method maintained the optoelectronic properties of the initial CMI raw powder, which will significantly promote the fabrication of Mo<sub>6</sub>-cluster-based optoelectronic devices in the future. Moreover, Renaud et al. recently proved that the Mo<sub>6</sub> cluster iodides are a new class of ambipolar materials [45], and the {Mo<sub>6</sub>I<sub>8</sub>}-based thin films (noted MI@FTO) fabricated via the EPD method have shown a significant application potential as a photoabsorber in an all-solid solar cell in the future. Moreover, Guy et al. used various Mo<sub>6</sub> clusters powders (Cs<sub>2</sub>Mo<sub>6</sub>Cl<sub>14</sub>, (TBA)<sub>2</sub>Mo<sub>6</sub>Br<sub>14</sub>, etc.) as precursors to synthesize Mo<sub>x</sub>N<sub>y</sub> nanomaterials with different compositions (Mo<sub>2</sub>N and Mo<sub>5</sub>N<sub>6</sub>) [46]. In contrast to the conventional synthesis using MoO<sub>3</sub> as a precursor, these Mo<sub>x</sub>N<sub>y</sub> products were prepared at lower temperatures and showed significant catalytic performances for the water–gas shift reaction.

In a previous study, we successfully produced MoS<sub>2</sub> from Mo<sub>6</sub>Br<sub>12</sub> powder as a precursor via two sulfurization processes [47]. Using the gas flow method, the sulfurization reaction occurred at 250 °C, but the product was a micron-sized amorphous MoS<sub>2</sub> powder. This reaction process still needs to be developed and the reaction mechanism better understood. Therefore, in this study, we decided to use this gas flow method combined with the EPD technology to establish a one-step sulfurization method at low temperature to fabricate a Mo cluster–MoS<sub>2</sub> thin film nanocomposite by using pre-prepared MI@FTO coatings as the precursor. The morphology and the reaction mechanism were investigated in detail. For future device applications, the obtained thin-film samples were carefully

evaluated for their  $\text{NH}_3$  gas sensing performance. The main results are reported and discussed.

## 2. Materials and Methods

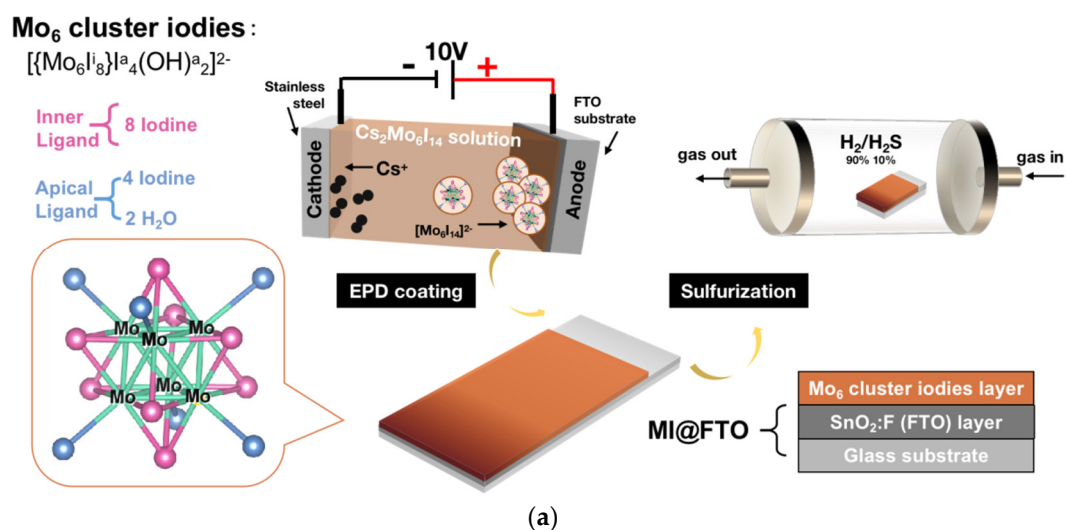
### 2.1. Chemicals

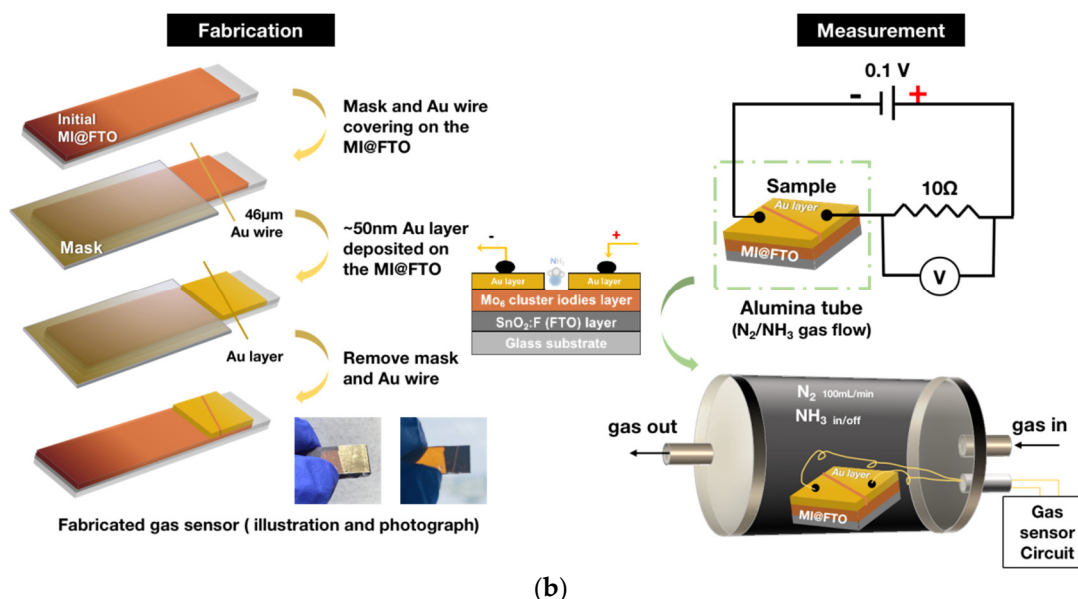
The synthesis path of the  $\text{Cs}_2\text{Mo}_6\text{I}_{14}$  initial powders via the solid-state method [48,49] and the MI@FTO films fabricated by using the EPD method [50] have been well established in our previous studies.

Briefly,  $\text{Cs}_2\text{Mo}_6\text{I}_{14}$  was synthesized by reacting CsI and  $\text{MoI}_2$  mixed and heated at  $700^\circ\text{C}$  for 4 days in a silica tube sealed under vacuum. For the EPD process, the  $\text{Cs}_2\text{Mo}_6\text{I}_{14}$  raw powder was dissolved in acetone (reagent-grade chemicals, 99.5%) at the concentration of 5 g per liter. The solution was then filtered using a  $0.2\ \mu\text{m}$  filter to remove any insoluble impurities. At the same time, the FTO glass substrate (Kenis Corp., Osaka, Japan) was cut into a  $25\ \text{mm} \times 10\ \text{mm}$  piece and washed in detergent and acetone for 30 min in an ultrasonic bath. Finally, the FTO substrate was used as the anode and immersed in a  $\text{Cs}_2\text{Mo}_6\text{I}_{14}$  cluster solution. The coating process was performed at 10 V for 5 min.  $\text{Cs}^+$  cations and  $[\{\text{Mo}_6\text{I}_8\}\text{X}^a_6]^{2-}$  ( $\text{X} = \text{I}, \text{OH}$ ) were deposited on the cathode and the FTO glass anode, respectively [45]. It should be noted that during the EPD coating process, the  $[\{\text{Mo}_6\text{I}_8\}\text{I}^a_6]^{2-}$ -cluster molecules will lose two iodide apical ligands, which were replaced by water ligands, as confirmed by the XPS result in a previously published report [45]. Accordingly, the final composition of the MI@FTO film in this study is described as  $[\{\text{Mo}_6\text{I}_8\}\text{I}^a_4(\text{H}_2\text{O})^a_2] \cdot x\text{H}_2\text{O}$ . The MI@FTO thin films deposited on the FTO substrate were used for the sulfurization process.

### 2.2. Sulfurization Process

All the sulfurization reactions were carried out in a tubular furnace with a flowing  $\text{H}_2/\text{H}_2\text{S}$  (90%/10%) mixture gas (99.9%, Air Liquid). The MI@FTO sample was initially placed in an aluminum boat, then into the furnace. The reaction chamber was purged with  $\text{N}_2$  gas for 30 min before the start of the reaction to ensure removal of the air, and the furnace was always at 1 atmospheric pressure. The  $\text{H}_2/\text{H}_2\text{S}$  gas was then introduced at the rate of 15 mL/min in the temperature range of  $250\text{--}450^\circ\text{C}$ , and the main reaction time was 1 h for all the MI@FTO films with the increasing rate of 5 degrees per minute. The  $\text{H}_2\text{S}$  acted as the sulfur source for the sulfurization reaction and the  $\text{H}_2$  acted as the reducing atmosphere to protect the cluster film from oxidation. An illustration of the EPD and the sulfurization process for the MI@FTO is shown in Figure 1a. According to the reaction temperature, the final products were denoted as MI-250, MI-300, etc. The reaction time was labeled for the specific sample, which is the extended reaction times, e.g., MI-350-3h.





**Figure 1.** (a) Illustration of MI@FTO prepared via EPD and sulfurization processes. (b) Illustration of the gas sensor fabrication and measurement.

### 2.3. Fabrication and Measurement of Gas Sensor

The fabrication and measurement of the MI@FTO gas sensor are illustrated in Figure 1b. This measurement was conducted by a chemiresistive gas sensor, which consisted of two electrodes connected to the sensing material. The change in resistance or current of the sensor device was measured in order to analyze the concentration of the target gas.

First, a 46  $\mu$ m Au wire covered the MI@FTO surface, and the covered area was used for the performance measurement. An approximately 50 nm Au layer was deposited on the exposed sample surface by a vacuum evaporator (VG Microtech E6700S, Newhaven, UK) to improve the surface conductivity. A Cu wire was connected from the Au-deposited area to the ampere-meter (Graphtec midi Logger GL240, Graphtec Corporation, Yokohama, Japan) to monitor and record the real-time current. The MI@FTO was placed in an alumina tube with flowing NH<sub>3</sub> gas (99.9%, Sumitomo Seika Chemicals, Tokyo, Japan) for the measurements.

### 2.4. Characterization

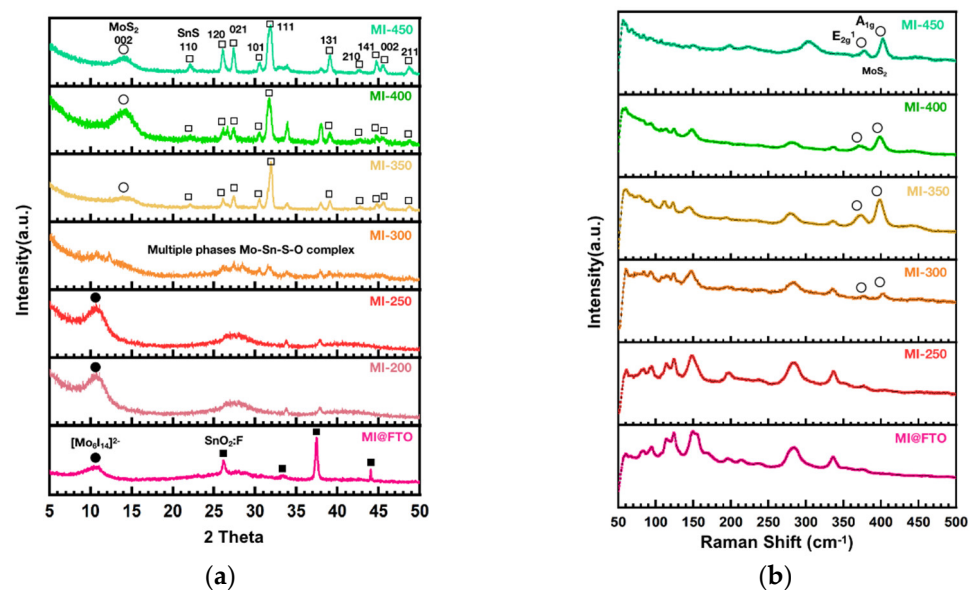
The structure and morphology of the thin-film samples, before and after sulfurization, were investigated by the grazing-incidence X-ray diffraction technique (GIXRD, SmartLab, Rigaku Corp., Tokyo, Japan) at room temperature using Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 50 mA and 40 kV power, and the incident beam was set at fixed critical w angles ( $0.2^\circ \leq w \leq 0.8^\circ$ ). The layered structures were analyzed by micro-Raman spectroscopy (HORIBA T64000, Kyoto, Japan) using a 515 nm laser source. The surface morphology and the elemental composition mapping of the thin-film sample were analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi SU4800, Tokyo, Japan) at 10–15 kV coupled with an energy-dispersive X-ray (EDX) analysis device, and high-resolution observations of the powder scratched from the thin-film sample were performed by a high-resolution transmission electron microscope (HRTEM, JEOL 2100F, Tokyo, Japan) equipped with an EDX analysis device. The electron binding energy spectra of the thin-film samples were measured by X-ray photoelectron spectroscopy (XPS, ULVAC Quantum-2000, Chigasaki, Japan) using Al K $\alpha$  radiation at 15 kV and 50 W and a take-off angle of 45°. All the binding energies were calibrated versus the C 1s peak of the adventitious carbon at 285 eV.

### 3. Results and Discussion

#### 3.1. Structure and Morphology

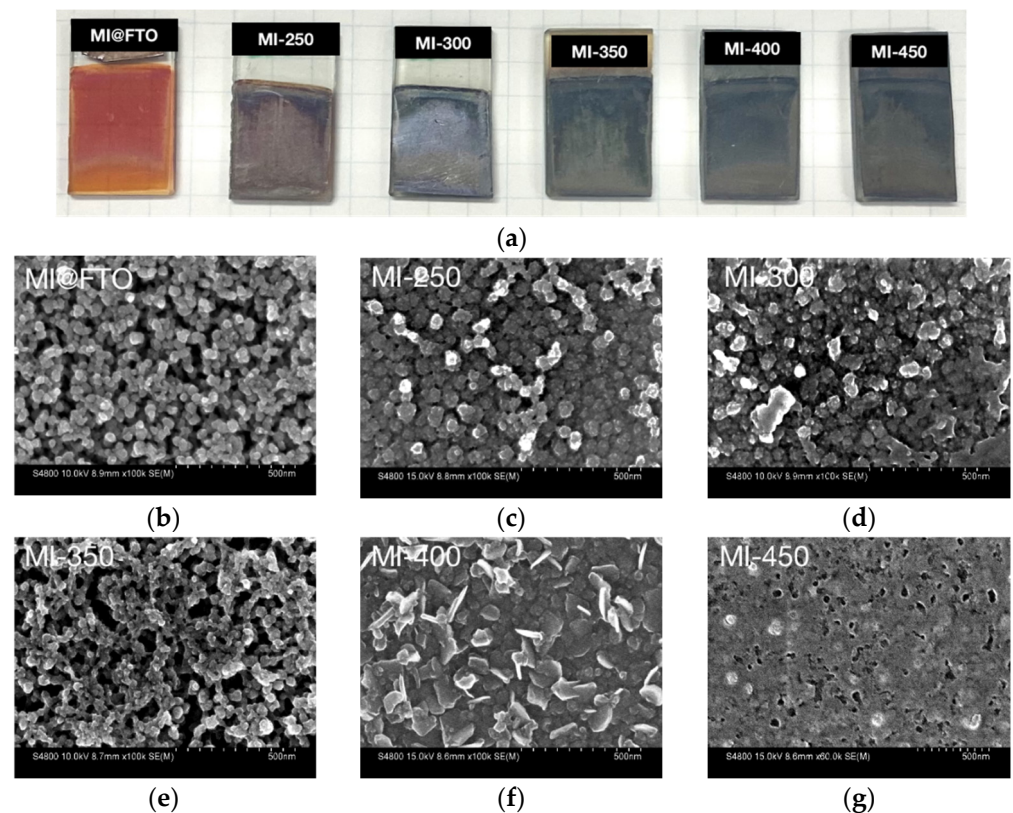
The GIXRD results in Figure 2a show the patterns of the initial MI@FTO and sulfurized samples. The wide peak observed around 9–12 degrees and the sharp crystal peaks at the higher  $2\theta$  angle in the initial MI@FTO pattern can be identified as the amorphous  $\text{Mo}_6$  cluster iodide film and  $\text{SnO}_2\text{:F}$  from the FTO substrate, respectively, which is consistent with our previous studies [45,51].  $\text{MoS}_2$  and  $\text{SnS}$  are found as the final products during this sulfurization process (see MI-450 pattern in Figure 2a). Indeed,  $\text{MoS}_2$  is the final product of the sulfurization reaction starting from the MI@FTO thin-film precursor occurring from 250 °C, and this result is consistent with the powdered  $\text{Mo}_6\text{Br}_{12}$  cluster precursor [47]. The wide peak initially measured around 9–12 degrees, due to the  $\text{Mo}_6$  cluster iodides, has shifted to 14 degrees upon increasing the temperature. This indicates that the  $\text{Mo}_6$  cluster iodide has entirely disappeared in favor of  $\text{MoS}_2$ . The presence of  $\text{SnS}$  crystals over 350 °C is unexpected. The  $\text{SnO}_2$  layer between the  $\text{Mo}_6$  cluster iodides and the  $\text{SiO}_2$  glass layer plays the role of the Sn source leading to  $\text{SnS}$  crystals at the end of the process. The pattern of MI-300 shows complex peaks of multiple phases. Considering that  $\text{SnO}_2$  may have been involved in the reaction, the product might contain the  $\text{Mo}_x\text{S}_y$  complex [52], the  $\text{Sn}_x\text{S}_y$  complexes [53], and also the Sn-Mo cluster complexes [54]. Additionally, the involvement of an O source derived from  $\text{SnO}_2$  may also have contributed to the formation of metal oxysulfide complexes [55]. In general, the FTO substrates are used as substrates for the synthesis of tin sulfides using the CVD method because the  $\text{SnO}_2$  surface is suitable for the growth of tin sulfides and does not participate in the reaction at such temperatures [56,57]. This fact implies that the excellent catalytic properties of the  $\text{Mo}_6$  cluster iodides promote the  $\text{SnO}_2$  layer in order to participate in the sulfurization reaction [57].

In contrast to the well-grown  $\text{SnS}$  crystal, the final product of the reaction, only one wide diffraction pattern present in the XRD patterns was used to confirm the formation of  $\text{MoS}_2$ . In the Raman spectrum (see Figure 2b), the  $\text{MoS}_2$  layered structure peaks are observed around 375  $\text{cm}^{-1}$  and 400  $\text{cm}^{-1}$ , which represent the in-plane vibration ( $E_{2g}^1$ ) and out-of-plane vibration ( $A_{1g}$ ), respectively, beyond 300 °C. It is indicated that the  $\text{Mo}_6$  cluster iodides, used as a precursor, are gradually sulfurized into the layered  $\text{MoS}_2$  structure, which is consistent with the wide peak around 14 degrees corresponding to the  $\text{MoS}_2$  (002) surface in the XRD pattern.



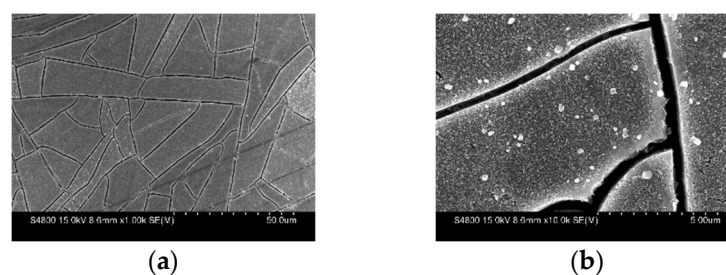
**Figure 2.** (a) GIXRD pattern of MI@FTO and sulfurized samples at different temperatures; (b) Raman spectra of MI@FTO and sulfurized samples under 515 nm excitation.

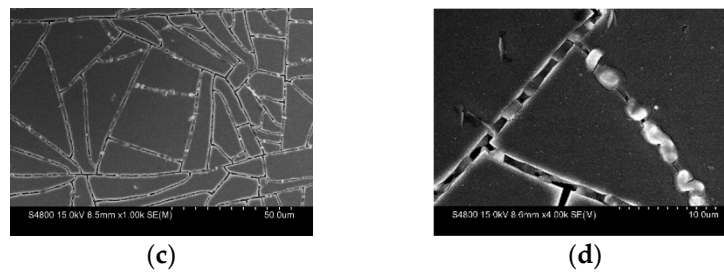
Figure 3a shows pictures of the initial MI@FTO and sulfurized samples at different temperatures. The initial MI@FTO film is a translucent orange film. During the sulfurization process, the color of the MI@FTO films undergo a change from orange to dark brown (MI-250) to dark gray with a metallic luster (from MI-300 to MI-450), which indicates that the sulfurization reaction occurs beyond 250 °C. The dark gray color of the metallic luster sample must also correspond to the MoS<sub>2</sub> and SnS phases. The surface morphology of the initial MI@FTO observed by FE-SEM and illustrated in Figure 3b shows isolated [ $\text{Mo}_6\text{I}_8\text{X}_6$ ]<sup>2-</sup> (X = I, OH) nanoparticles with diameters around 20–50 nm up to 300 °C. As the temperature increases to 350 °C, the nanoparticles are sintered into a continuous porous structure.



**Figure 3.** Pictures and FE-SEM observation with the scale bar at 500 nm of MI@FTO and sulfurized samples: (a) photographs of samples on a squared paper (5 mm × 5 mm); (b) initial MI@FTO; (c) MI-250; (d) MI-300; (e) MI-350; (f) MI-400; (g) MI-450.

At 400 °C, the surface morphology becomes nanoflaked with a surface area around 100 nm<sup>2</sup>. At the same time, the isolated bulk crystal around 500 nm in size is also observed on the surface, as shown in Figure 4a,b. When the temperature increases to 450 °C, the surface becomes bumpy. Isolated crystals and cracks can also be observed on the surface, as shown in Figure 4c,d.





**Figure 4.** SEM observation of (a) MI-400 with the scale bar at 50  $\mu\text{m}$ ; (b) MI-400 with the scale bar at 5  $\mu\text{m}$ ; (c) MI-450 with the scale bar at 50  $\mu\text{m}$ ; (d) MI-450 with the scale bar at 10  $\mu\text{m}$ .

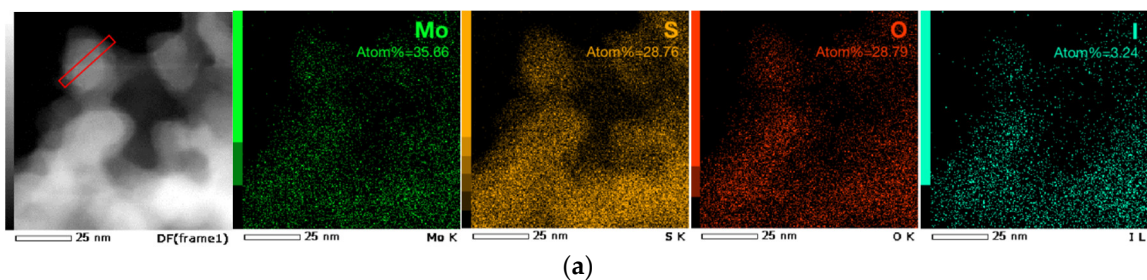
These results illustrate that there are two reactions occurring during the sulfurization of MI@FTO, i.e., one starting at 250  $^{\circ}\text{C}$ , when the  $\text{Mo}_6$  clusters are sulfurized, leading to  $\text{MoS}_2$ ; one starting at 350  $^{\circ}\text{C}$ , not only when the  $\text{Mo}_6$  cluster sulfurization reaction occurs, but also when the  $\text{Mo}_6$  clusters catalyze the sulfurization of  $\text{SnO}_2$  into  $\text{SnS}$ .

### 3.2. Mechanism of the MI@FTO Sulfurized into $\text{MoS}_2$ and $\text{SnS}$ crystal Growth Hypothesis

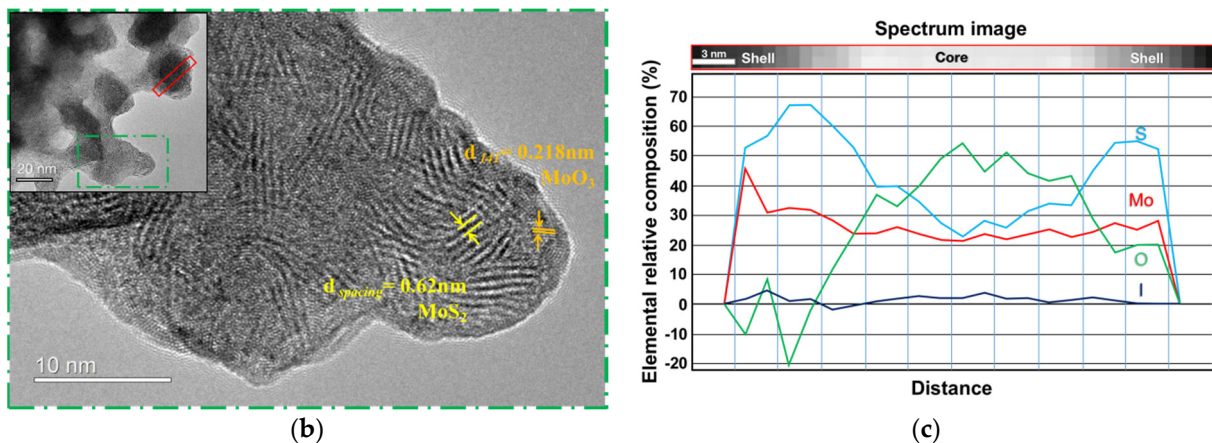
In order to clarify the sulfurization mechanism of the  $\text{Mo}_6$  cluster iodides, the MI-250 powder samples were scratched from the films for HRTEM observations (see Figure 5) in order to exclude interference from the FTO substrate and provide an easy sample preparation.

It is noteworthy that the EDX analysis in Figure 5a demonstrates that the MI-250 contains Mo, S, O, and I elements, but not the Sn element, which means that  $\text{SnO}_2$  is not involved in the reaction below 250  $^{\circ}\text{C}$ . The high-resolution analysis of the O element in the nanoparticle revealed that the Mo is oxidized. In addition to the  $\text{MoS}_2$  layer structure, the  $\text{MoO}_3$  crystal structure is also observed in Figure 5b. Moreover, the electron energy loss spectroscopy (EELS) analysis in Figure 5c revealed that there is a high concentration of Mo and S elements in the shell of the MI-250 nanoparticles but just a little oxygen. Conversely, the core contains a small amount of S and a high concentration of the Mo and O elements. This fact shows that, first, the film-bound water during the EPD process [45,58] serves as the O source, suggesting that the initial  $\text{Mo}_6$  cluster iodide is probably oxidized into  $\text{MoO}_3$ . The  $\text{H}_2\text{S}$  gas then serves as the S source for the subsequent sulfurization to produce  $\text{MoS}_2$  on the nanoparticle surface.

It has been reported that  $\text{MoO}_3$  can play the role of a precursor on the FTO substrates at low temperatures to be sulfurized into  $\text{MoS}_2$ . On the other hand,  $\text{SnO}_2$  in the FTO coating is stable and does not participate in the reaction even when the temperature increases to 700  $^{\circ}\text{C}$ ; thus, the final product, the  $\text{MoS}_2$  sulfurized from the  $\text{MoO}_3$  precursor, would not contain  $\text{SnS}$ . [59]. This fact confirms that the  $\text{MoO}_3$  used as a mid-product in this study is not the key material that catalyzes the  $\text{SnO}_2$ :F layer on the FTO substrate to generate  $\text{SnS}$  under the  $\text{H}_2/\text{H}_2\text{S}$ .



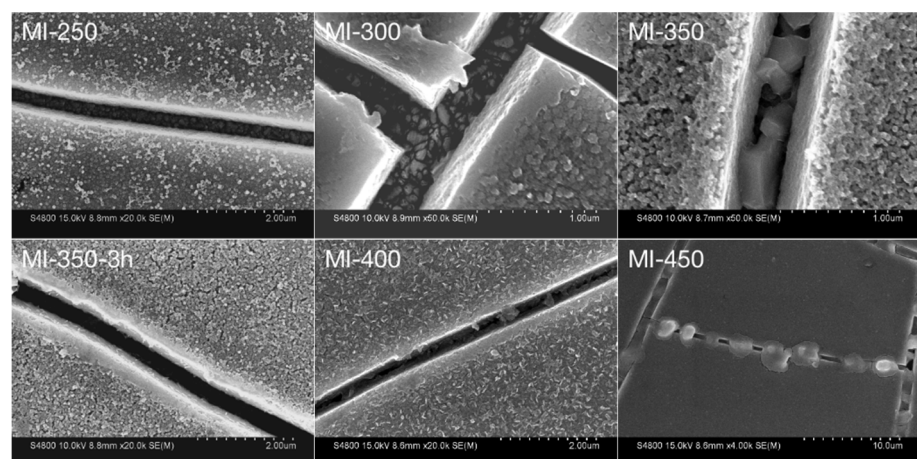




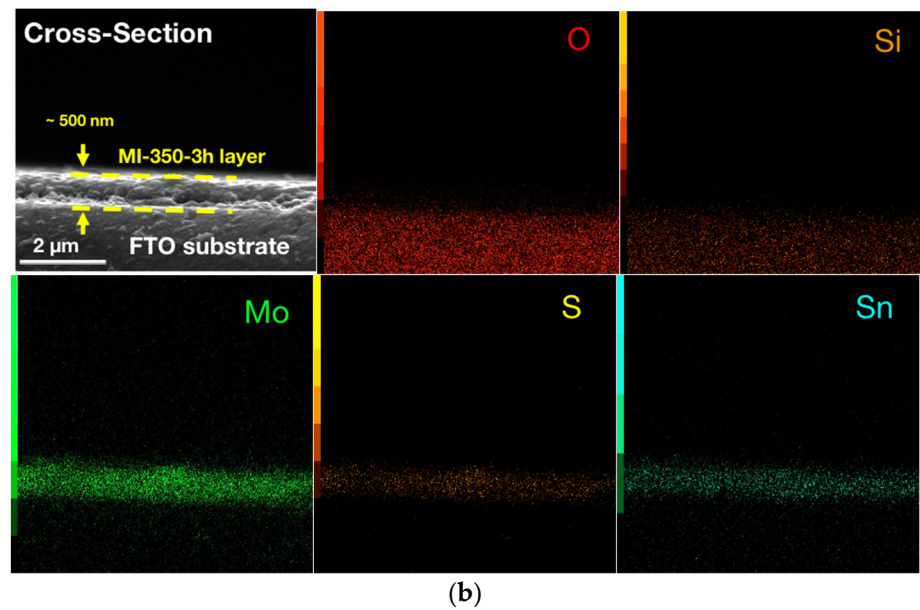
**Figure 5.** HRTEM observation of MI-250 powder scratched from thin films with the same observation area is marked in the figure. (a) Element mapping from HRTEM equipped with EDX device with the scale bar at 25 nm, and the elemental quantitative result is marked; (b) HRTEM image of MI-250; (c) EELS analysis of the MI-250 nanoparticles.

Our study is the first report showing that  $\text{Mo}_6$  cluster iodides deposited on FTO substrates can generate SnS at 350 °C without external Sn sources, indicating that the  $\text{Mo}_6$  cluster iodides have a catalytic role. Although the reaction mechanism is still unclear, we attempted to provide some explanations for the growth of the SnS crystals. Figure 6a shows the FE-SEM observation focusing on the crack of the thin-film samples at different temperatures. The main morphology starting from the  $\text{Mo}_6$  cluster iodide nanoparticles is consistent with the observation shown in Figure 3. At high temperatures, cracks inevitably occur in the MI@FTO films, and the appearance of the cracks exposes the  $\text{SnO}_2$  layer to the  $\text{H}_2/\text{H}_2\text{S}$  gas flow and concomitantly to the  $\text{Mo}_6$ -cluster-iodide-based layer. Multiple  $\text{SnS}_x$  phases are observed by heating of the blank FTO, free of  $\text{Mo}_6$  cluster iodides, starting from 350 °C (see Figure S1). However, the SnS crystals grow well from the exposed  $\text{SnO}_2$  surface and are catalyzed by the  $\text{Mo}_6$  cluster iodides at MI-350, and MI-400 also shows the bulk SnS crystal around 500 nm.

Based on this result, we extended the sulfurization time to 3 h (i.e., MI-350-3h), and the morphology of MI-350-3h still retains the shape of the nanoparticles with a diameter of about 50 nm, but these particles are sintered together. Figure 6b shows a cross-section of the MI-350-3h film sample with the presence of Sn that highlights the migration of the Sn in the Mo layer and a very uniform doping. This indicates that the  $\text{SnO}_2$  layer reacts with the  $\text{Mo}_6$  cluster iodide along the layer, not only on the top surface.



(a)

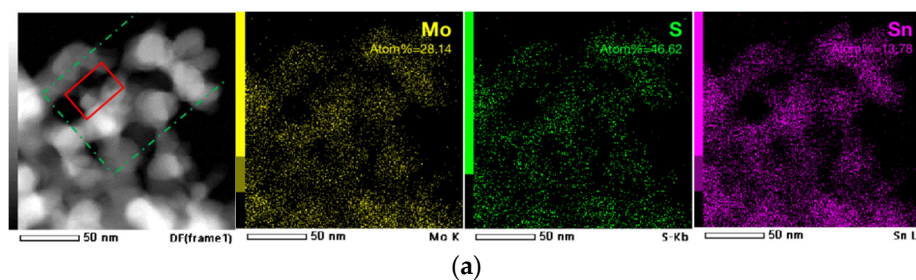


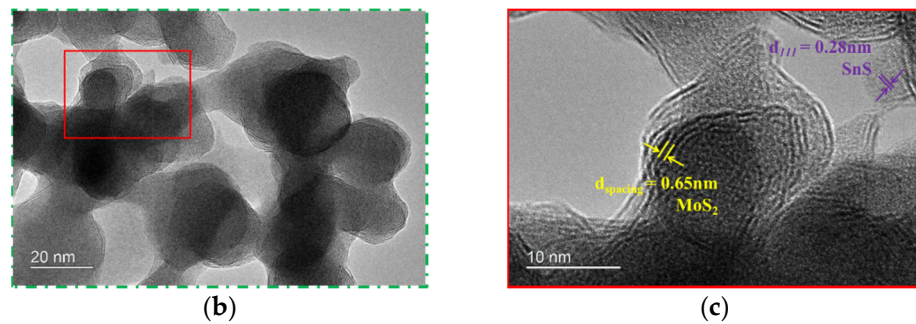
**Figure 6.** SEM observation of thin-film samples: (a) the cracks and (b) the cross-section of MI-350-3h.

The MI-350-3h powder samples were also scratched from the films for the HRTEM observations (see Figure 7). The layer spacing of the 2D structure is 0.65 nm, which is consistent with MoS<sub>2</sub>. In addition, the lattice spacing of the nanocrystal structure is 0.28 nm, which is consistent with the (111) plane of SnS from the XRD results. The element mapping clearly shows the uniform distribution of the Mo, Sn, and S elements in the sample.

It is noteworthy that the EDX elemental quantitative analysis result shows that the content of the I element in MI-350-3h is  $I\% = 0.07$ , while in the MI-250 sample,  $I\% = 3.24$ . The content of the I element is much lower than those of the Mo and S elements in the sulfurized MI@FTO sample as the sulfur replaces the iodine ligand in the Mo<sub>6</sub> cluster unit to form the Mo<sub>x</sub>S<sub>y</sub> cluster. The Mo cluster structure gradually decomposes to form MoS<sub>2</sub>, which is the final product. The I<sub>2</sub> gas generated by the decomposed Mo<sub>x</sub> ( $1 \leq x \leq 6$ ) cluster iodides reacts with H<sub>2</sub>/H<sub>2</sub>S and leaves the reaction chamber as a by-product in the gas flow. The Mo<sub>6</sub> cluster iodides and I<sub>2</sub> gas by-product during decomposition of the Mo<sub>x</sub> cluster ( $1 \leq x \leq 6$ ) may play an important role here to catalyze the SnO<sub>2</sub>:F layer to the SnS crystal.

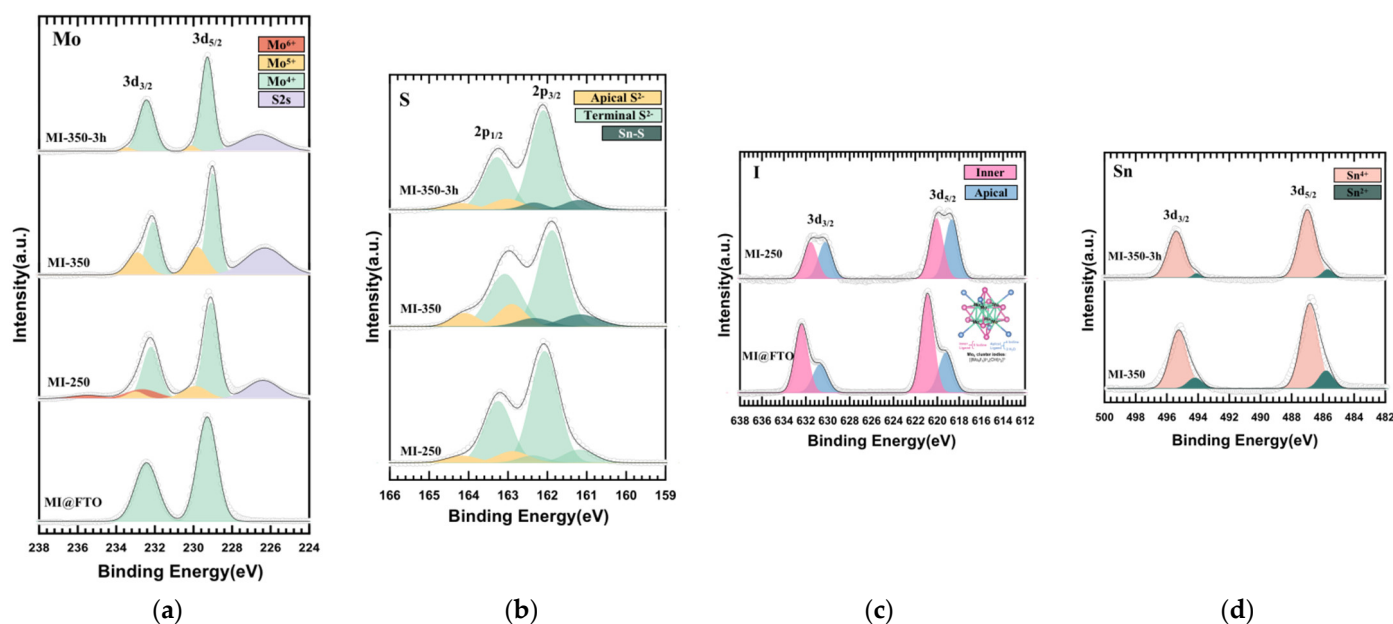
The generation of halogen gas by-products during the sulfurization of the Mo<sub>6</sub> clusters has also been reported in our previous studies [47]. By using the chemical vapor transport (CVT) method, the Mo<sub>6</sub>Br<sub>12</sub> and sulfur powder were mixed and sealed in a quartz vacuum tube for the sulfurization reaction; the Br<sub>2</sub> gas and MoBr<sub>3</sub> by-product are retained in the tube and affects the pressure of the vacuum tube reaction system, which affects the final product, MoS<sub>2</sub>, as a 3D-formed nanosheet or single crystal.





**Figure 7.** HRTEM observation of MI-350-3h powder scratched from thin film; the same observation area is marked in the figure. (a) Element mapping from HRTEM equipped with EDX device with the scale bar at 50 nm, and the elemental quantitative result is marked; (b) HRTEM image of MI-350-3h with the scale bar at 20 nm; (c) scale bar at 10 nm.

Figure 8 shows the XPS results of four thin-film samples, i.e., MI@FTO, MI-250, MI-350, and MI-350-3h. One Mo  $3d_{5/2}$ - $3d_{3/2}$  doublet peak is identified in the Mo 3d spectrum for the initial MI@FTO with binding energies of 229.3 eV–232.4 eV, suggesting the  $\text{Mo}^{4+}$  states. Moreover, two I  $3d_{5/2}$ - $3d_{3/2}$  doublet peaks in the I 3d spectrum with a ratio of 2:1 are observed, which is consistent with our earlier research and correspond to the ratio of the inner ligands to apical ligands in the  $[\{\text{Mo}_6\text{I}_8\}\text{I}_4(\text{H}_2\text{O})_2]$  cluster molecular structure combining  $\text{H}_2\text{O}$  molecules [45,60]. Three Mo  $3d_{5/2}$ - $3d_{3/2}$  doublet peaks are attributed to the  $\text{Mo}^{4+}$ ,  $\text{Mo}^{5+}$ , and  $\text{Mo}^{6+}$  states for MI-250. According to the HRTEM result of MI-250, the  $\text{Mo}^{4+}$  states can be attributed to the  $\text{MoS}_2$  layered structure, whereas the  $\text{Mo}^{5+}$  states correspond to the  $\text{Mo}_x\text{S}_y$  clusters [61–64]. Finally, the  $\text{Mo}^{6+}$  doublet peak must be due to  $\text{MoO}_x$ , which is produced from the MI@FTO and bound water. Two doublet peaks are observed in the MI-250 I 3d spectrum with a ratio of roughly 1:1. The presence of the I 3d peak is not only consistent with the EDX elemental quantitative analysis result of the MI-250 sample (see Figure 5a), but the two doublet peaks representing the inner ligand and apical ligand also suggest that MI-250 contains a minor amount of molybdenum iodide sulfide clusters [65]. The three S  $2p_{3/2}$ - $2p_{1/2}$  doublet peaks present in the MI-250 S 2p spectrum should all belong to the Mo-S compounds because MI-250 is devoid of Sn. The terminal  $\text{S}^{2-}$  in  $\text{MoS}_2$  is indicated by a major doublet at the binding energies of 162.1 eV–163.3 eV. On the other hand, a minor doublet is assigned to the apical/bridge S at the slightly higher binding energies of 162.9 eV–164.2 eV, which belong to the  $\text{Mo}_x\text{S}_y$  phase with the  $\text{Mo}^{5+}$  state. An additional terminal  $\text{S}^{2-}$  doublet peak is also recognized as a minor doublet observed at the lower binding energies of 161.2 eV–162.4 eV. These low-binding energies are caused by the effect of  $\text{H}_2$  during the synthesis [66].



**Figure 8.** XPS result of MI@FTO, MI-250, MI-350, and MI-350-3h thin films: (a) Mo 3d spectrum; (b) S 2p spectrum; (c) I 3d spectrum; (d) Sn 3d spectrum.

In the MI-350 and MI-350-3h samples, no  $\text{Mo}^{6+}$  state, representing  $\text{MoO}_x$ , is found in the Mo 3d spectrum. The I 3d peak also disappears, proving that  $\text{MoO}_x$  as an intermediate product is completely sulfurized. The content of the  $\text{Mo}^{5+}$  ions in the product significantly decreases when the sulfurization time increases from 1 to 3 h, demonstrating that the  $\text{Mo}_x\text{S}_y$  cluster phase gradually produces  $\text{MoS}_2$  that is compatible with the Raman results.

Two Sn 3d  $3d_{5/2}$ - $3d_{3/2}$  doublet peaks are observed in the Sn 3d spectrum of MI-350 and MI-350-3h, suggesting the  $\text{Sn}^{4+}$  and  $\text{Sn}^{2+}$  states.  $\text{Sn}^{4+}$  is associated with the Sn-doping into the  $\text{MoS}_2$  complex and the  $\text{SnO}_2$  substrate combined with the HRTEM results obtained for MI-350-3h, whereas the  $\text{Sn}^{2+}$  state corresponds to the SnS crystals. In the S 2p spectrum, the doublet peak corresponds to the Sn-S bonds. These results demonstrate that the  $\text{SnO}_2$ -coated layer in the FTO substrate begins to take part in the reaction and synthesizes SnS, which is consistent with the XRD results, in which the  $\text{Mo}_6$  clusters demonstrate their outstanding catalytic capabilities.

Based on this result, the sulfurization reaction of the  $\text{Mo}_6$  cluster iodide thin films can be described as follows: first, the  $\text{Mo}_6$  clusters acquire bound water during the EPD coating, and the bound water reacts with the  $\text{Mo}_6$  cluster iodides at 250 °C to form  $\text{MoO}_x$ ; subsequently,  $\text{MoO}_x$  is sulfurized into  $\text{MoS}_2$  by  $\text{H}_2\text{S}$ . In this process, the iodide ligand is gradually replaced by sulfur ligands and the  $\text{Mo}_6$  clusters are gradually decomposed. When the reaction temperature becomes higher or the reaction time becomes longer, the final product is the layered  $\text{MoS}_2$ . Thus, the composition of the MI-250 thin film should be the  $\text{MoO}_x$ - $\text{Mo}_x\text{S}_y$  cluster- $\text{MoS}_2$  composite with doped iodide.

On the other hand, the main component of MI-300 should be a metal sulfide (oxysulfide) complex of Mo and Sn, while the components of MI-350 and MI-350-3h should be SnS- $\text{MoS}_2$  nanoparticles. The MI-350-3h thin film has a porous sintered particles morphology. The distribution of the Mo and Sn elements is, thus, uniform, which is obtained at such a low synthesis temperature. Although the reaction mechanism of  $\text{SnO}_2$  catalyzed by  $\text{Mo}_6$  cluster iodides to form SnS is not known, it is worth further research.

### 3.3. $\text{NH}_3$ Sensor Application

Ligated  $\text{Mo}_6$ -cluster-containing compounds used for sensing activity are currently limited to oxygen sensor [67,68], pH sensing [69], biological sensing [70], and photo-response [58,71]. According to theoretical calculations, such compounds are predicted to have a good selectivity for  $\text{NH}_3$  in the NRR [29]. Previous studies have also demonstrated

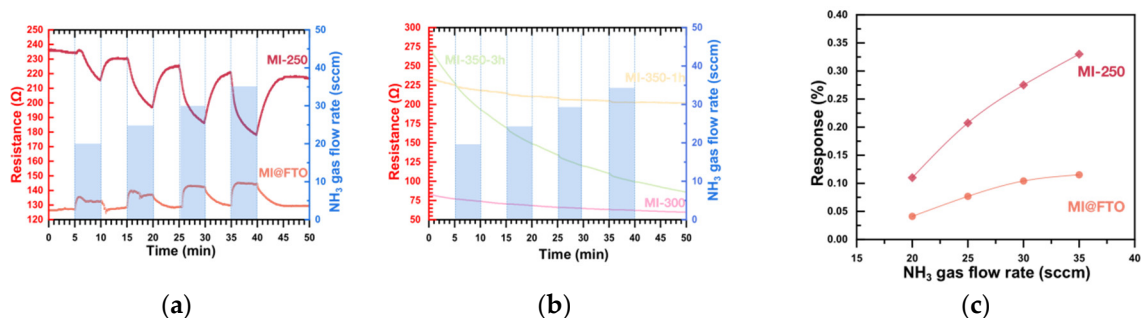
that they exhibit a photo-response and can react with  $\text{NH}_3$  to form  $\text{Mo}_x\text{N}_y$  species at 400 °C [46,58,71]. Thus, we inferred that  $\text{Mo}_6$  cluster iodides should have a specific adsorption of  $\text{NH}_3$  even at room temperature and that this adsorption could cause a potential change when a voltage is applied to the MI@FTO, which was proved to be an ambipolar material ( $E_g = 1.9$  eV). In addition, the nanoparticle morphology of the material could also increase the specific surface area and, thus, enhance the adsorption effect. Based on these facts, a simple MI@FTO sensor was designed and fabricated to verify this hypothesis (see Figure 1b).

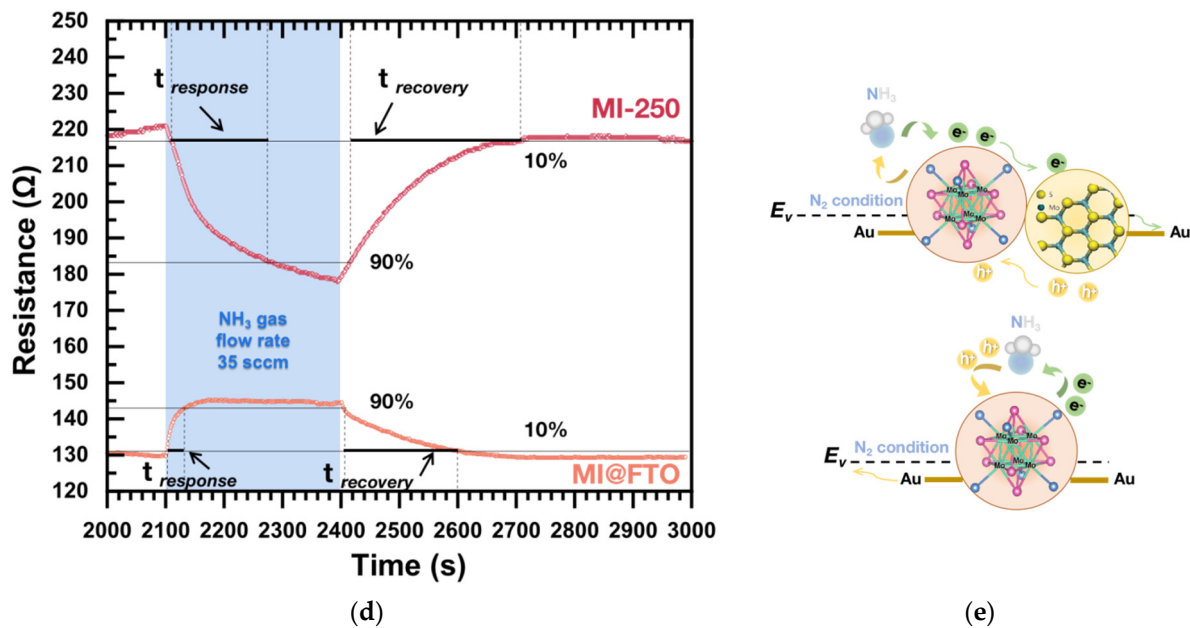
The MI@FTO and sulfurized sample gas sensors were carefully tested at room temperature, 1 atmosphere, and in shaded light in order to investigate the sensing performance of  $\text{NH}_3$  under a  $\text{N}_2$  atmosphere for its potential applications in gas detection. The flow rate of the  $\text{N}_2$  gas stream was constant at 100 sccm. The flow rate of the  $\text{NH}_3$  gas was adjusted to achieve a change in the concentration of  $\text{NH}_3$  in the atmosphere. Its real-time current change was detected with the voltage of 0.1 V by flowing  $\text{NH}_3$  gas in the alumina tube. The gas sensing response (%) was calculated using the following equation:

$$\text{Response}(\%) = \frac{|I_g - I_0|}{I_0} \times 100\% = \frac{\Delta I}{I_0} \times 100\% \quad (1)$$

where  $I_0$  is the base current, and  $I_g$  refers to the corresponding current with the  $\text{NH}_3$  gas exposure.

Figure 9a shows the result of the  $\text{NH}_3$  sensing performance of the initial MI@FTO and MI-250 samples. The initial MI@FTO with the pure  $\text{Mo}_6$  cluster iodide film was, for the first time, used as a gas sensor and demonstrated a significant responsiveness. Gas sensing mechanisms can be interpreted as electron (or hole) transport between a sensing film and the target gas via charge transfer. Depending on whether the gas is oxidizing or reducing (e.g.,  $\text{NH}_3$ ) and the sensing film is a p- or n-type semiconductor, electrons are withdrawn from or donated to the sensing film, which would cause the resistance of the sensing material to increase or decrease [72–74]. The initial MI@FTO shows an increased resistance when exposed to  $\text{NH}_3$  gas, while MI-250 shows a decrease in resistance, proving that MI@FTO shows the behavior of a p-type semiconductor, while MI-250 is an n-type conductor (see Figure 9e). This conversion could be the result of a sulfur defect and iodine doping [75–77].





**Figure 9.** NH<sub>3</sub> sensing performance of (a) MI@FTO, MI-250; (b) MI-300, MI-350, and MI-350-3h thin films; (c) calculated response of the MI@FTO and MI-250 gas sensor corresponding to gas flow rate of NH<sub>3</sub>; (d) transient response and recovery times of NH<sub>3</sub> (35 sccm) for MI@FTO and MI-250 gas sensor; (e) schematic illustration of MI-250 gas sensor (top) and MI@FTO gas sensor (bottom) for NH<sub>3</sub> under N<sub>2</sub> condition.

The other samples (e.g., MI-300, MI-350-1h, and MI-350-3h) that contain Sn also exhibit the n-type characteristics but with a slight (or no) responsiveness to NH<sub>3</sub> (see Figure 9b), even poorer than the MI@FTO, which may be due to the decomposition of the Mo cluster, thus reducing the activity site. The XRD results show that the composition of MI-300 is an extreme complex of Mo-Sn metal oxysulfur compounds, and the gas detector of MI-300 does not exhibit any selectivity for NH<sub>3</sub> gas. For the MI-350-1h and MI-350-3h samples, XRD results show that the main component of the product is MoS<sub>2</sub>, which indicates that the Mo<sub>6</sub> cluster structure has been largely decomposed and the SnS nanocrystal has been generated together, while the macrostructure of the material changes into a porous sinter. Both MI-350-1h and MI-350-3h show a poorer selectivity for NH<sub>3</sub> compared to the initial MI@FTO, which may be mainly due to the decomposition of the Mo<sub>6</sub> cluster. During the gas sensor measurements, most of the samples, including MI-350-3h, very quickly stabilize their resistance in ambient N<sub>2</sub>, while MI-350-1h continues to reduce its resistance in the ambient N<sub>2</sub>, proving, on the one hand, that it is also an n-type semiconductor, and on the other hand, it has a high capacity for adsorption than selectivity. This result is consistent with the XPS Mo 3d spectrum, which shows that MI-350-1h has more Mo<sup>5+</sup> components compared to MI-350-3h, meaning that it has more active sites.

It is worth noting that when the sulfurization temperature is above 400 °C, the SnO<sub>2</sub> layer in the FTO substrate will be destroyed and mixed into the sample (the HRTEM image of MI-400 is shown in Figure S2). Thus, the samples, which were sulfurized beyond 400 °C, were not made into a gas sensor for measurements.

Figure 9c shows the responses of MI@FTO and MI-250 based on different NH<sub>3</sub> gas flow rates. As the measurement circuit is at a constant voltage (0.1 V), the response calculated for the current is actually equivalent to the rate of change of the sample's resistance. The response is taken as an absolute value for the comparison; MI-250's response rate improves 3 times versus that of the MI@FTO (11% to 31%) at an NH<sub>3</sub> rate of 35 sccm. The increase in the response rate should be attributed to the activity sites provided by the Mo cluster [29] and the core-shell structure of MoO<sub>3</sub>-MoS<sub>2</sub> [78], and probably attributed to the p-n heterojunction structure [79] between the Mo<sub>6</sub> cluster and MoS<sub>2</sub>.

Based on the XRD results, the components of MI-250 can be described as a p-type  $\text{Mo}_x$  cluster ( $x \leq 6$ ) and sulfurized n-type  $\text{MoS}_2$  (and also  $\text{MoO}_x$ ). The XPS I 3d spectrum of MI-250 also shows two clear doublets, proving that the  $\text{Mo}_6$  cluster core is still present. Recently, it has been reported that when the  $\text{Mo}_6$  cluster iodide is immobilized on p-type graphene ( $\text{Mo}_6@$ Graphene), this nanohybrid material exhibits a sensitivity to  $\text{NO}_2$  gas but not  $\text{NH}_3$  gas when made into the chemiresistive gas sensor. The response of  $\text{Mo}_6@$ Graphene to  $\text{NH}_3$  is even lower than the response of the initial graphene to  $\text{NH}_3$ , because the  $\text{NH}_3$  cannot exchange charges, and only few positive charges (hole) are transferred from the p-type graphene layer toward the  $\text{Mo}_6$  cluster [80]. These results demonstrate that the sulfurization strategy is effective in enhancing the  $\text{NH}_3$  gas response of the  $\text{Mo}_6$  cluster iodide, probably due to the p–n heterojunction structure between the  $\text{Mo}_6$  cluster and  $\text{MoS}_2$ .

After the sulfurization process, the resistivity of the samples shows a good linear relationship at different temperatures (see Figure S3). It means that the sulfurized  $\text{Mo}_6$  cluster layer has good ohmic contact with the FTO electrode. Based on that, the resistance change of the gas sensor while it is exposed to the target gas can be reflected due to the negligible contact resistance at the interface. It is worth pointing out that the resistance of MI-250 and MI-300 varies very little with temperature (a small increase with temperature), which indicates that MI-250 has good stability as a gas sensor. In contrast, the resistance of MI-350, MI-350-3h, and MI-400 decreases rapidly as temperature rises, indicating that they have a high potential for future thermosensitive applications.

Figure 9d, based on Figure 9a, shows the response time and recovery time of MI@FTO and MI-250 at the  $\text{NH}_3$  gas flow rate of 35 sccm. The response time was measured from the resistance point of the sample increasing by 10% to 90% of an end point (the maximum resistance point), while the sample was exposed to the target gas, and the recovery time was measured at the point where the resistance decreased from 90% of an end point to the 10% resistance point after the target gas was turned off. The response and recovery times for the  $\text{NH}_3$  detection at 35 sccm by the MI@FTO are 29 s and 198 s, respectively. In comparison, the MI-250 response and recovery times are 174 s and 254 s, respectively, both significantly lower than the performance of the MI@FTO. MI@FTO's fast response and recovery are attributed to its  $\text{Mo}_6$  cluster core [29].

After the gas sensor measurement, the final resistance of all the samples in this 45-min long test does not go back to zero when the  $\text{NH}_3$  gas turns off, which may be due to the fact that the sensor surface is not fully cleaned and some  $\text{NH}_3$  is still adsorbed. This behavior may be related to operating temperature and gas flow rate.

The sulfurization process starting from the  $\text{Mo}_6$  cluster iodides as the precursor leading to the expected  $\text{MoS}_2$  product and their  $\text{NH}_3$  sensing enhancement is evidence that this novel synthesis strategy is feasible. The transition of the  $\text{Mo}_6$ -cluster-iodide-based films from p-type to n-type semiconductors due to sulfurization reactions also opens up new design possibilities for future device applications, such as p–n junctions.

#### 4. Conclusions

This study established a simple and efficient method for the synthesis of Mo cluster- $\text{MoS}_2$  nanocomposites, which not only demonstrates the feasibility of sulfurizing  $\text{Mo}_6$  cluster iodides as precursors to generate  $\text{MoS}_2$ , but also directly allows the synthesis of nanocomposite thin films in just one step. This study also explored the performance of  $\text{Mo}_6$  cluster iodides and Mo cluster- $\text{MoS}_2$  nanocomposites as gas sensors for the first time. It was proved that the  $\text{Mo}_6$  cluster iodide gas sensor for  $\text{NH}_3$  at room temperature responds as a p-type semiconductor. After the sulfurization process at low temperature (250 °C), the response to  $\text{NH}_3$  gas increased by three times while the conversion from the p-type semiconductor to n-type occurred. Our results obtained in this study show the possibilities of  $\text{Mo}_6$  clusters and Mo-cluster-based  $\text{MoS}_2$  material for future applications.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano13030478/s1>, Figure S1: GIXRD pattern of FTO substrate sulfurized at different temperatures; Figure S2: HRTEM observation of MI-400 powder scratched from thin film; the same observation area is marked in the figure (a) HRTEM image of MI-400 with the scale bar at 100 nm; (b) scale bar at 10 nm; (c) Element mapping from HRTEM equipped with EDX device with the scale bar at 25 nm; Figure S3: Electrical measurements of the sulfurized samples at different temperatures, with a blank FTO substrate inserted at the top right as a reference.

**Author Contributions:** M.Z. conceived and designed the project; performed the EPD coating, sulfurization, characterization (Micro-Raman, FE-SEM, HRTEM, and XPS), gas sensor fabrication, and gas sensor measurement experiments; analyzed and interpreted the corresponding data; drafted the article; F.G. conceived and designed the project, performed the sulfurization and characterization (GIXRD) experiments, and revised the manuscript; A.R. performed the EPD coating and revised the manuscript; N.D. and S.C. conceived and designed the metal clusters chemistry and revised the manuscript; T.S. and Y.M. performed the gas sensor fabrication and gas sensor measurement experiments and revised the manuscript; T.K.N.N. performed the EPD coating and revised the manuscript; D.B. and J.-F.H. directed the project and revised the manuscript; T.U. conceived, designed, and supervised the project, and revised the manuscript. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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